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Elution of Ions from Melting Snow
Chromatographic Versus Metamorphic Mechanisms

James H. Cragin, Alan D. Hewitt and Samuel C. Colbeck   July 1993

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Abstract

Columns of natural and laboratory-aged snow grains and frozen water droplets were washed with deionized distilled water and with synthetic precipitation solutions to investigate both snowpack chemical fractionation and preferential ion elution. Concentrations of Cl^-, NO_3^- and SO_4^{2-} in sequential fractions of the column's eluate showed no chromatographic effects, indicating that ice crystals do not possess selective affinity for inorganic anions. Consequently, preferential chemical elution previously observed in melting snow is not caused by snow acting as a chromatographic column. Additional column experiments involving elution from frozen solution drops and from aged snow showed that both fractionation and preferential elution were strongly influenced by ion exclusion during the snow crystal growth.

Cover: Theoretical depiction of chemical changes occurring during snow metamorphosis.

CRREL Report 93-8
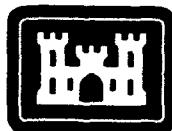
**US Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

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Elution of Ions from Melting Snow
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JAMES H. CRAGIN, ALAN D. HEWITT AND SAMUEL C. COLBECK

INTRODUCTION

When snow melts, the concentration of solutes in the meltwater is not constant but varies with time: the initial 30% of meltwater contains 50–80% of the total solutes in the snow (Johannesssen et al. 1975, Johannessen and Henriksen 1978). This phenomenon, now technically referred to as "fractionation" or the "ionic pulse," can contribute to the episodic spring acidification of streamwater, colloquially called "acid flush." The highly concentrated ionic pulse has been the focus of several laboratory (Colbeck 1981, Bales et al. 1989) and field (Williams and Melack 1991) studies which have shown enhanced ionic concentrations in meltwater from snow that has been subjected to melt–freeze cycles.

A more recently observed phenomenon is "preferential elution" within the highly fractionated initial snowpack meltwater; that is, not all ions are enriched to the same extent and some ions elute or are removed sooner than others. This process was first reported by Davies et al. (1982) and has been extensively investigated experimentally by Brimblecombe, Davies, Tranter, and co-workers at the University of East Anglia and University of Southampton, United Kingdom. Although the specific order of elution varies with the age of the snow and its chemical composition, NO_3^- and SO_4^{2-} generally appear in meltwater fractions before Cl^-. The composition of meltwater has been modeled in terms of the mixing of two different liquid solutions: a highly concentrated surface brine and a more dilute solution derived from snow-grain interiors (Brimblecombe et al. 1988).

While this model is useful, it does not describe the physical or chemical mechanisms that produce such a two-phase system.

The exact cause of preferential elution is still poorly understood. One proposed mechanism is that there are chromatographic effects when meltwater percolates through a snowpack (Tranter et al. 1986). In other words the snowpack itself acts as an ion chromatograph, with ice grains selectively retaining and retarding the elution of certain ions (e.g., Cl^-) over others (e.g., NO_3^- and SO_4^{2-}). The extent and strength of this sorption depends upon the physical and chemical properties of both the sorbed species and the substrate. As a substrate, ice can sorb molecular vapors such as SO_2 and NO_x from the atmosphere (Valdez et al. 1987), but whether ice can sorb inorganic ions from meltwater is unknown.

Another mechanism proposed by Hewitt et al. (1989) is that preferential chemical elution in meltwater is a result of preferential ion exclusion from snow grains during snow metamorphosis. When snow undergoes metamorphosis, some individual ice crystals grow larger at the expense of others (Colbeck 1987). While these grains are growing, chemical constituents are being incorporated into and excluded from the ice crystals with different efficiencies. This produces mature snow grains with a nonhomogeneous distribution of ions. When snow containing these mature grains melts, ions are released or eluted sequentially with time, and the resulting elution order is related to the exclusion efficiency of different ions imposed by the recrystallization process.

In this report we present results of experiments conducted to evaluate the importance of both chromatographic and metamorphic processes upon snowpack elution chemistry. Columns of naturally and laboratory-aged snow and artificial ice pellets were washed with solutions of deionized distilled water and the eluate collected in sequential fractions. This process simulates the removal of ions from metamorphosed snow grains by rainwater percolation through a snowpack, and has been shown (Tranter et al. 1992) to be analogous to the percolation of snow meltwater itself.

METHODS

All plastic, glass, and stainless steel laboratory utensils used for snow collection, grain growth, sample storage and analysis were thoroughly cleaned as described previously (Hewitt et al. 1989, 1991).

Chemical analysis

Analyte concentrations were determined using a flame (FAA) and graphite furnace (GFAA) atomic absorption spectrophotometer, an ion chromatograph and a pH electrode. The small (1-mL) aliquot restricted analysis volumes to 200 μL per instrumental technique.

Sodium concentrations were determined by FAA with a Perkin-Elmer model 403 spectrophotometer. To reduce sample volumes, 100-μL aliquots were injected into a conical vial before aspiration into the burner chamber. Potassium, calcium and magnesium were determined by GFAA with the same spectrophotometer and a Perkin-Elmer model 2200 heated graphite atomizer. Precision of FAA and GFAA measurements was ±10% or better.

Anions were determined with a Dionex model 2010i ion chromatograph, equipped with an HPICE-AS3 separator column, AFS 1–2 anion fiber suppressor and 50-mL sample loop. The eluant was 3-mM $NaHCO_3$/2.4-mM Na_2CO_3 and the regenerate was 12.5-mM H_2SO_4, flowing at 2.9 mL/min and 3.0 mL/min, respectively. The determination of ammonium ion was also performed by ion chromatography. For this analysis a HPIC CS–1 separator column, CFS 1–2 cation fiber suppressor, and 100-μL loop were employed. The eluant was 7.5-mM HCl, with a flow rate of 2.3 mL/min, and the regenerate was 0.04 M $Ba(OH)_2$, with a flow rate of 3.0 mL/min. Precision of ion chromatographic analyses was ±5%.

Hydrogen ion concentrations were determined to within ±0.02 pH unit using an Ml–410 micro-combination pH electrode (Microelectrodes, Inc.). Quiescent 100-μL aliquots were measured after the elec-

trode was calibrated with low ionic strength buffers (Orion).

Analytical standards for the determination of Cl, NO_3^- and SO_4^{2-} were prepared from NaCl, KNO_3 and $(NH_4)_2SO_4$ (Baker, reagent grade). The concentration of the working standards and the determination of pH were verified daily by the analysis of the National Institute of Science and Technology simulated rain water reference standards, SRM–2694 1&11.

Snow collection

Snow used in these experiments was collected on two separate occasions from a rural location in Hanover, N.H.: one fresh snowfall in January after an overnight precipitation event and another in March from a two-month-old snowpack. The fresh snow was composed of a mixture of submillimeter needles and irregular crystals, while the aged snow consisted of rounded 1- to 2-mm grains. The fresh snow was used for metamorphosis experiments while the aged grains were used for the chromatographic experiments.

Natural and synthetic snow grains—chromatographic experiments

Bulk compositions of the naturally aged snow samples and the solution used for the frozen drops are given in Tables 1 and 2, respectively. Artificial ice beads were made by freezing 10-μL drops of either Milli-Q (Millipore Corp) deionized water or this water spiked with nitric acid, ammonium chloride and ammonium sulfate to produce the concentrations shown in Table 2. The water droplets were frozen on polyethylene sheets in a Class 100 clean air station located inside a coldroom at –12°C. The frozen hemispherical drops weighed an average of 6.4 mg, with the loss of mass being attributed to sublimation. Deionized water or deionized water spiked with nitric acid and ammonium salts representative of precipitation were employed as column eluants (composition given in Table 3).

Laboratory grain growth—metamorphism experiments

Fresh snow was aged with an imposed temperature gradient in 1-mm-thick butyrate plastic cylindrical columns (3.7-cm O.D. × 55-cm length) fitted with polyethylene end caps. These columns were filled after mechanically mixing the snow and passing it through an 18-mesh (1.3 mm) polypropylene sieve. The desegregated snow crystals ($\approx$ 0.3 to 1.3 mm) were poured through a large funnel into the growth columns, which were agitated while filling

Table 1. Bulk ionic composition of homogenized natural snow used for chemical elution experiment.

Ion	Concentration (μeq/L)
H^+	22 (pH = 4.7)
Na^+	13.5
K^+	0.4
Ca^{2+}	2.9
Mg^{2+}	0.8 $\Sigma^+ = 40$
Cl^-	14.8
NO_3^-	17.7
SO_4^{2-}	10.6 $\Sigma^- = 43$

Table 2. Composition of solution used to prepare synthetic snow grains.

Ion	Concentration (μeq/L)
H^+	100 (pH = 4.0)
NH_4^+	114
Cl^-	14.3
NO_3^-	100
SO_4^{2-}	104

Table 3. Composition of eluant solution used for anion chromatographic experiment.

Ion	Concentration (μeq/L)
H^+	10 (pH=5.0)
NH_4^+	28.7
Cl^-	2.8
NO_3^-	16.1
SO_4^{2-}	20.8

to facilitate uniform packing. The snow transfer operation was performed at the opening of a clean air station housed in a –2.2°C coldroom. Four columns were sequentially filled as described above to a 50-cm depth, resulting in densities of 226 ±7 kg/m³. Additionally, three subsamples of the sieved snow were collected for determination of the bulk snow chemical composition.

The filled grain-growth columns were taken to a –20°C coldroom and placed in an insulated temperature gradient apparatus (Fig. 1). This apparatus positioned the columns at equal distances from the walls and from one another inside a 20-cm–I.D. cardboard Sono tube. The spaces between the four cylindrical cavities were filled with urethane foam insulation and covered at both ends with rigid Styrofoam (Dow Chemical Co.) insulation. Once all four

Figure 1. Schematic (not to scale) of experimental arrangement used for aging snow. The base of the columns was maintained at –2°C with a heating pad while the top of the columns was at the temperature of the coldroom, –20°C.

grain growth columns had been fitted into the cavities of the grain growth apparatus, a plastic bag was put over the top of the Sono tube to protect against particle contamination, and additional fiberglass insulation (9 cm thick × 56 cm wide) was wrapped three times around the vertical walls. The grain growth apparatus was positioned on an aluminum plate, 0.6 cm thick × 20 cm O.D. Centered below the aluminum plate and on top of a large rectangular 5-cm-thick Styrofoam board was a thin (≈ 1.0-mm thick × 1.8-cm O.D.) heating pad. Current to the heating pad was controlled with a rheostat. The temperature of the aluminum plate was monitored with a 9-cm–long, 3-mm-diameter needle probe thermocouple that fitted snugly into a hole drilled radially into the aluminum plate. Throughout the grain growth experiment, the rheostat was set to maintain a temperature of –2 ± 1°C within the aluminum plate, producing a temperature gradient between the top and bottom of the growth columns of approximately 36°C/m. (Such a temperature gradient can be found in snowpacks in the western U.S. and Canada.) Temperature readings were taken at least daily. Individual growth columns were removed after periods of 7, 14, 28, and 56 days, and similar placebo columns filled with loosely packed fiberglass insulation were inserted into the vacant cavities to maintain thermal balance.

Once removed, columns were placed on a clean polyethylene sheet inside a clean air station within the –20°C coldroom. Taking precautions not to disturb the fused snow grains, we cut the column into two sections with a razor knife, resulting in a lower 15-cm portion (bottom ⅓) that had been adjacent to the aluminum plate and an upper 35-cm (top ⅔) portion. The snow from each section was then trans-

ferred to polyethylene bottles. The bottle containing snow from the bottom 15 cm was shaken to disaggregate the fused grains. Subsamples of the dispersed snow grains were taken for microscopic crystal identification and for bulk snow chemical determinations. Most of the remainder was used for elution experiments.
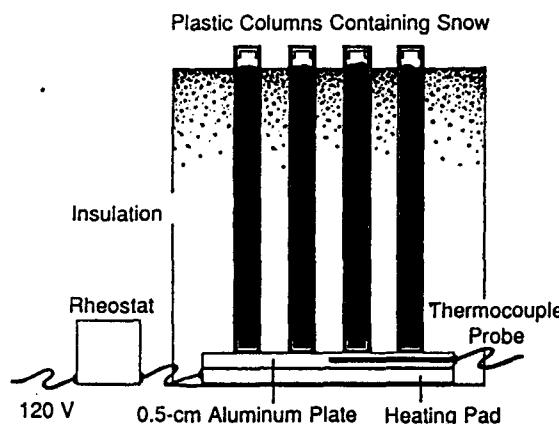
Column elution

The flow of meltwater or rainfall through snow was simulated using a 1.8-cm-diameter × 30-cm-long glass column (Fig. 2) filled with natural or laboratory-grown snow grains, and frozen solutions of deionized water drops. The column was made by replacing the stopcock of a Pyrex 100-mL burette with a plastic three-way stopcock. A 5-cm^3 plastic Luer-Lok (Becton Dickinson) syringe was connected to the horizontal port of the three-way valve. Teflon tubing attached the stopcock to the glass column and to the syringe. The vertical path of the three-way stopcock transferred aliquots of the column eluant to a 1.5-mL collection vial (Perkin-Elmer sample cup).

Column elution experiments were conducted within a Class 100 clean air station in a 0°C coldroom. At the start of an experiment the aqueous solutions passed onto the columns were at 1° ±1°C. Eluant solution flow of 0.57 mL/min onto the col-

Figure 2. Schematic (not to scale) of apparatus used for chemical elution experiments.

umn was metered with a syringe pump (Sage Instrument Co.). The eluant (deionized water or deionized water spiked with dilute acids and salts) appeared to wet the surfaces of all snow grains. Column eluate was removed by suction created by the syringe. Volumes ranging between 100 and 300 μL were drawn off the column through the three-way stopcock into the section of tubing attached to the syringe. The three-way stopcock was then turned so that this aliquot could be injected into a collection vial. Once the vial contained 1 mL it was removed and emptied into a 7.5-mL CPE polyethylene bottle. The collection vial was rinsed with deionized water between samples. After eluant application onto the column was stopped, only a single additional aliquot could be obtained. The total surface areas for the natural snow grains and the frozen droplets contained within the column were approximately 0.14 m^2 and 0.10 m^2, respectively.

RESULTS AND DISCUSSION

Chromatographic experiments

Three different types of column elution experiments were conducted for this portion of the study using 1) natural snow grains eluted with deionized water, 2) frozen solution drops eluted with deionized water and 3) frozen deionized water drops eluted with synthetic salt solutions.

For the first experiment the elution column was filled with homogenized, aged snow (1- to 2-mm grains). The bulk chemical composition of this snow, as determined by triplicate analysis, is given in Table 1. Deionized water was applied at a rate of 0.57 mL/min to the top of the column and 1-mL aliquots of eluate were collected at the bottom. Concentratio. s of cations (Fig. 3) and anions (Fig. 4) were as much as 4.5 times as high in the initial eluate as in the bulk snow itself. Divalent ions (calcium, magnesium and sulfate) were fractionated to a greater extent than univalent ions. The high initial concentrations decrease exponentially and appear to stabilize after the eighth aliquot. The concentration of the least fractionated ion, chloride, shows the smallest change and was always less than the bulk snow concentration, most likely because of dilution by the applied deionized water. Other ions were also diluted by the deionized water, reducing their concentrations in the eluate so that the actual enrichment (fractionation) would have been appreciably higher if the snow grains had been allowed to melt naturally. Using deionized water for elution reduced the time of the experiment from an estimated 10–12 hours to about 30 minutes. Of the five cations stud-
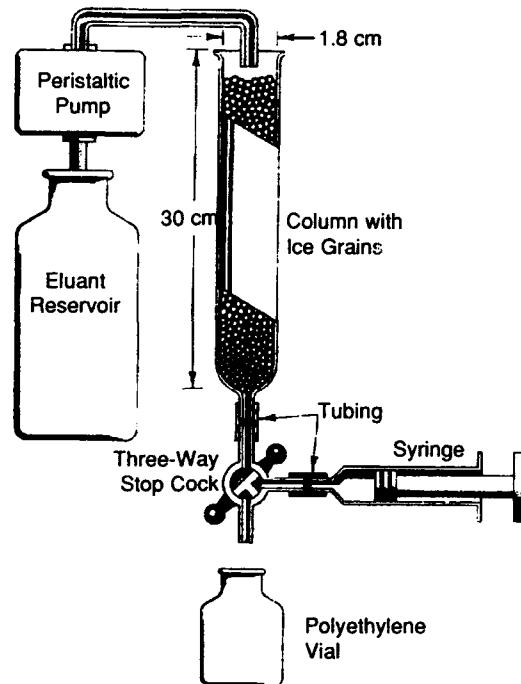
4
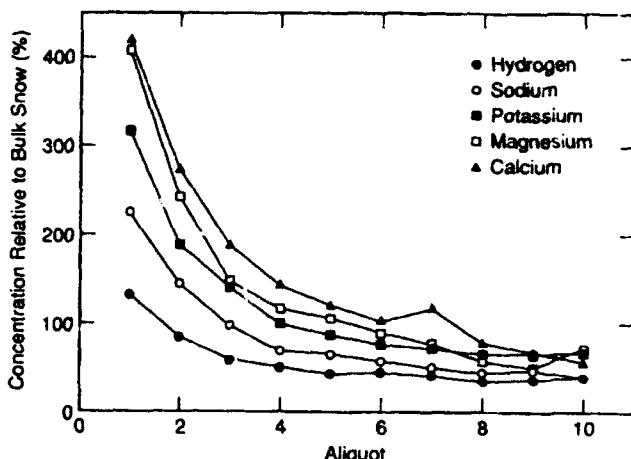
Figure 3. Normalized cation concentrations in sequential eluate aliquots for natural snow elution. Concentrations have been normalized to bulk snow concentrations.
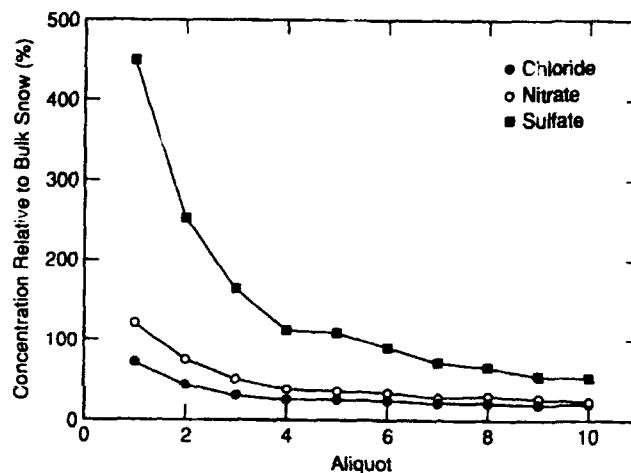

Figure 4. Normalized anion concentrations in sequential eluate aliquots for natural snow elution.

ied, hydrogen ion shows the least relative enrichment (Fig. 3); other constituents, especially divalent ions, are fractionated to a greater degree. On a molar basis hydrogen ion is the major ion in fractionated meltwater because it is the dominant ion in snow itself (see Table 1).

The effects of chemical fractionation are clearly shown in Figures 3 and 4 and, while preferential elution is apparent, it is more clearly seen in Figure 5 where ionic ratios show the early elution of sulfate, and to a lesser degree nitrate, relative t hloride. Notice that the ratios plotted in Figure 5 have been normalized to the corresponding ratios in the bulk snow so that even with the high enrichments (fractionation) of initial aliquots, sulfate and nitrate appear earlier (elute earlier or preferentially) than chloride.

As an indirect check on the accuracy of our analytical methods and to determine if we measured all major constituents present in the snow, anion/ cation ratios were calculated and are plotted in Figure 6. Ideally, this ratio should be unity for ionic balance and electroneutrality. Generally, the ratio is near unity but with a slightly decreasing trend from

1.1 for the first aliquot to about 0.8 for the tenth aliquot. While some of the deviation could be attributed to experimental error (±5% for each ion) this effect should be random and is not expected to produce an apparent trend. Alternatively, since the ratio decreases with aliquot, an unanalyzed cation may be present later in the elution sequence. An
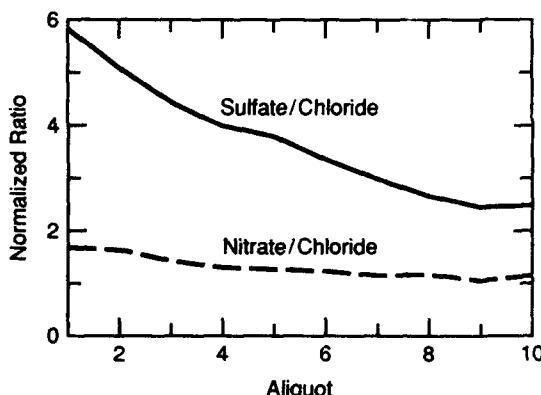

Figure 5. SO_4^{2-}/Cl^- and NO_3^-/Cl^- ratios in sequential eluate aliquots for natural snow elution. These ratios are normalized to the corresponding ratios in bulk snow.

5
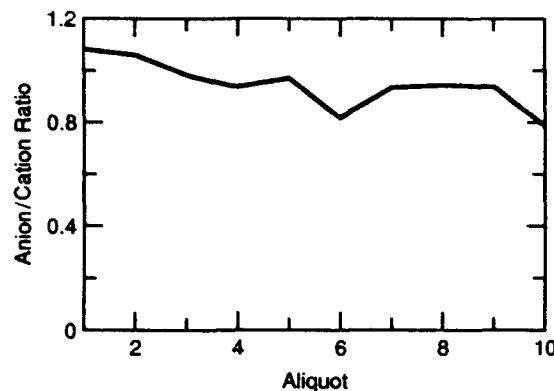
Figure 6. *Ion balance for natural snow elution. Anion/cation ratios were calculated from summed concentrations in* μeq/L.
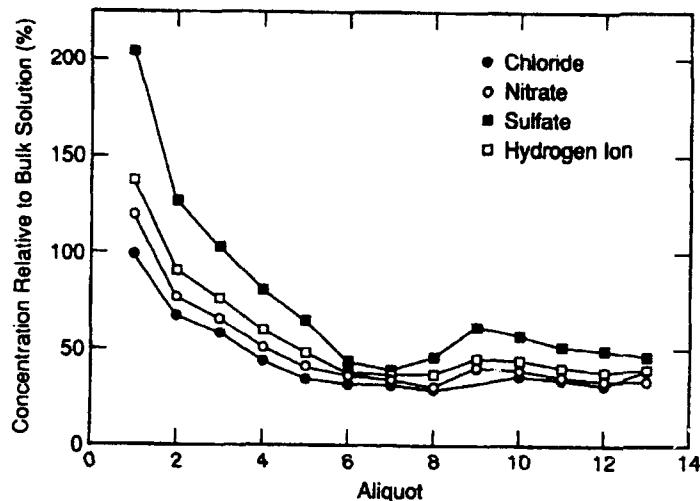

Figure 7. *Normalized anion concentrations in sequential eluate aliquots for elution from frozen solution drops.*

obvious choice of cation would be N H₄, but the concentrations we determined were too low to explain the observed differences. This decreasing anion/cation ratio has also been observed in natural snow samples by others and has been tentatively attributed to dissolved forms of organic carbon.*

To simulate the process of fractionation and preferential elution in the laboratory, we prepared synthetic snow grains by freezing droplets of a solution containing ions at the concentrations shown in Table 2. These concentration levels are typical cf acid snow for the northeastern United States. The column was filled with approximately 5000 frozen hemispherical droplets of this solution and, as with the natural snow grains in the previous experiment, eluted by slowly passing deionized water downward. Concentrations in the eluate (Fig. 7) are initially high (2-fold for SO_4^{2-}) and decrease rather rapidly as elution progresses. The fact that the relative chloride concentration in the first aliquot is 100% (i.e., the same as the bulk snow) is fortuitous and simply indicates that any fractionation present was offset by dilution with the deionized water used for elution.

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Again, fractionation (Fig. 7) and preferential elution (Fig. 8) are occurring but to a smaller extent than in natural snow grains. For example, sulfate shows only a two-fold enrichment over chloride for the frozen solution drops (Fig. 8) instead of the six-fold enrichment for natural snow.

From the previous two experiments it was not possible to distinguish if the observed preferential elution was caused by an actual chromatographic sorption mechanism or if it was due to the fact that the initial meltwater from ice grain surfaces had a different composition than the later meltwater from inner grain material, as recently proposed by Brimblecombe et al. (1987, 1988). The third type of elution experiment was designed specifically to determine whether or not snow has ion chromatographic properties. This experiment was essentially the reverse of the second experiment: instead of percolating distilled water through frozen solution drops, a synthetic solution (Table 3) representative of natural precipitation was allowed to flow through a column of frozen distilled water drops.

Results of this experiment are shown in Figure 9 for the three anions studied. As in any chromatographic analysis, the column was first conditioned

Figure 8. Normalized SO_4^{2-}/Cl^- and NO_3^-/Cl^- ratios in sequential eluate aliquots from frozen solution drops.
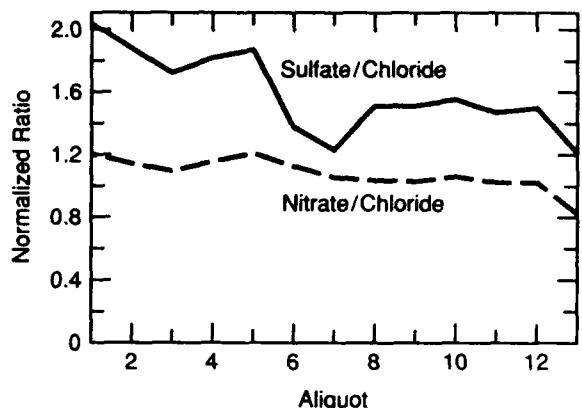
Figure 9. Normalized anion concentrations in sequential eluate aliquots for chromatographic experiments using frozen deionized water drops. Arrows on the abscissa indicate the beginning and the end of application of synthetic snow solution. Prior flow was due to application of deionized water.
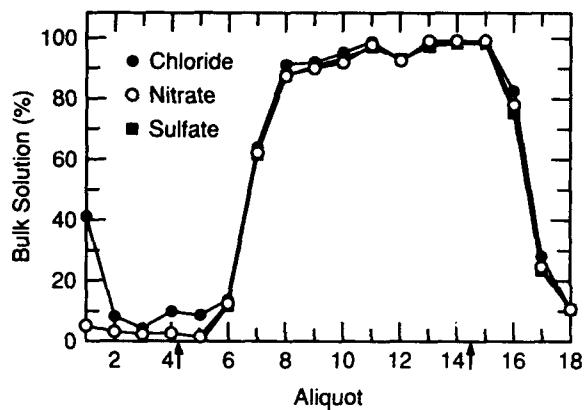
Figure 10. Normalized SO_4^{2-}/Cl^- and NO_3^-/Cl^- ratios in sequential eluate aliquots for chromatographic experiment where synthetic snow solution was allowed to flow over frozen distilled water drops. Arrows on the abscissa are the same as for Figure 9.
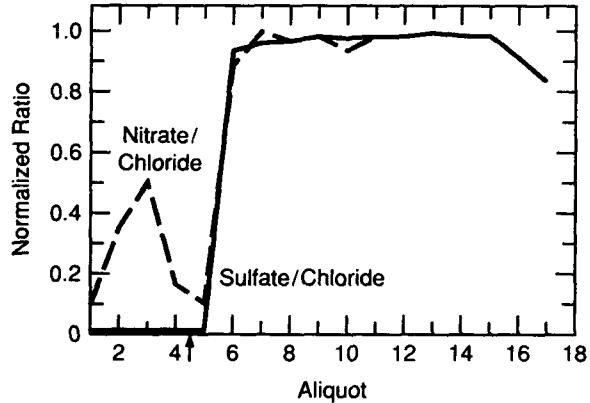
with a carrier fluid, in this case deionized water. The synthetic snow solution was treated as a "sample" in standard chromatographic analysis, "injected" and then allowed to flow downward through the column. Sample flow into the column started between collection of the fourth and fifth aliquots as indicated by the arrow on the abscissa. After a short period of sample application the eluant was then switched back to deionized water (second arrow on abscissa of Fig. 9). The high concentration of chloride in the

first aliquot was due to a small but finite amount of impurity (2.2 µg Cl⁻/L) in the deionized water used to prepare the frozen droplets used in the column. Chloride in the deionized water was excluded as the drop froze and was forced to the surface, making it available for rapid initial release from the elution column.

Shortly after the synthetic precipitation solution was applied, concentrations of all three anions in the eluate rose simultaneously to that of the bulk solu-

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Figure 11. Original snow used for metamorphosis/elution experiments consisting of 0.1- to 0.3-mm rounded crystals. Rounding of fresh snowflake arms and angularities occurred during isothermal storage at –20°C for several days.

Figure 12. Snow crystals aged for one week with an imposed temperature gradient of 36°C/m. Sample taken from bottom third of column 1. Crystals are larger (0.2–0.4 mm) than original snow and have developed some angularity.

Figure 13. Snow crystals aged for two weeks. Sample taken from bottom third of column 2. Crystal size ranges from 0.5 to 0.7 mm.

Figure 14. Snow crystals aged for four weeks. Sample taken from bottom third of column 3. Crystals are larger (up to 2 mm), sintered and faceted.

Figure 15. Snow crystals aged for eight weeks. Sample taken from bottom third of column 4. Crystals are as large as 3 mm, sintered and highly faceted. Many hexagonal, cup-shaped depth-hoar crystals are present, like the one in the lower center of photo.

Figure 16. Snow crystals aged for eight weeks. Crystals are from top two-thirds of column 4. Crystals are 0.3–1 mm in size and some faceting (see hexagonal plate in lower right) is apparent, although most crystals are rounded due to the slower growth rates because of the lower temperature in the upper section of the column. This material is similar in appearance to snow aged for one week in the bottom third of column 1 (see Fig. 12).

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tion and remained at this level until deionized water was reapplied. Throughout the experiment all normalized concentrations paralleled each other very closely and were even identical for many of the aliquots. Normalized ionic ratios (Fig. 10) were constant and essentially unity in the eluate of the synthetic solution. All three ions eluted simultaneously (i.e., no preferential elution), indicating that sorptive chromatographic effects are absent for these three anions.

Metamorphism experiments

If it is not chromatographic, what, then, is the cause of preferential chemical elution in snowpack meltwater? Previously, Tsiouris et al. (1985) observed preferential chemical elution from snow grains that had been aged for one year in a coldroom. But the same snow sample showed no preferential chemical elution when it was originally collected. This indicates to us that preferential elution is related to processes occurring during snow metamorphosis. We hypothesize that selective exclusion of ions during grain growth, whether occurring in a coldroom or natural snowpack, produces mature snow grains that have enriched chemical concentrations on the surface compared to the interior. Although growth of grains in dry snow occurs from the vapor (no melting is required), the exclusion of ionic salts is analogous to the rejection of ions from a slowly freezing salt solution. Because different ions are excluded with different efficiencies, the ionic ratio in the surface portion of growing grains is different from that within the grain interior and the bulk snow itself. This preferential exclusion may be the result of steric incompatibility of ions within the ice lattice itself. Both fractionation and the order of preferential chemical elution are consistent with this hypothesis. To test this hypothesis, we aged fresh snow under an imposed temperature gradient for various lengths of time and then conducted elution experiments to determine the effect of grain growth upon the degree of fractionation and preferential elution.

Figures 11–15 show the effect of aging (metamorphosis) upon the snow crystals. The original starting material (Fig. 11) for the experiment consisted of small (0.1- to 0.3-mm) crystals and crystal fragments whose apexes became slightly rounded during the time between sample collection and experiment initiation due to the higher vapor pressures at sharp curvatures (Kelvin effect). After one week of aging with an imposed 36°C/m temperature gradient (Fig. 12), crystals in the bottom of the column had developed some angularity and had grown to 0.2 to 0.4 mm, while after two weeks (Fig. 13) crys-

tal growth was more extensive (0.5 to 0.7 mm) and the crystals are angular with hexagonal plates beginning to appear. After four weeks (Fig. 14) the crystals are much larger ($\approx$ 1 mm), faceted, and beginning to sinter. The final sampling, taken after eight weeks (Fig. 15), contains large (up to 3 mm), sintered, highly faceted crystals, many of which are hexagonal and cup-shaped, similar to depth-hoar.

To show the effect of temperature upon crystal growth, the top two-thirds of column 4 was sampled (Fig. 16). Although this material was under the same temperature gradient as that in the bottom third of the column, the average temperature was –14°C as compared to –5°C for the bottom third. The crystals in the upper section of the column are smaller (0.3 to 1 mm) than those in the bottom section (3 mm) and, while some faceting is apparent, most are still rounded because of the slower growth rates at the lower temperature in the upper section of the column. This material is similar in appearance to that present in the bottom third of column 1 (see Fig. 11).

While the snow crystals are undergoing metamorphic physical changes, concurrent chemical changes are taking place as well. Figure 17 shows sulfate, hydrogen, nitrate and chloride ion concentrations in sequential elution aliquots for the snow crystals aged in columns. The aging times of 1, 2, 4, and 8 weeks are the same as the crystals in the photographs of Figures 12 through 15.

Chemical fractionation (higher ionic concentrations in initial meltwater) and preferential elution (some ions are enriched more than others) are readily apparent in Figure 17. Our explanation is that both these phenomena result from ion exclusion during snow grain metamorphosis. Figure 18 shows this concept schematically. Assume that all crystals have similar initial (time t_1) solute distributions. As the snowpack ages and vapor is transferred from warmer to colder crystals (Colbeck 1987), the concentration of impurities increases for the shrinking grains (time t_2) until they have completely disappeared (time t_3), leaving their impurities upon the surfaces of the mature grains. At the same time, the larger grains are growing, selectively rejecting chemical species within the newly developed layers of ice lattice. This rejection is energetically favorable because impurities located on ice grain surfaces or at disordered grain boundaries cause less strain than if they are located within the ice matrix itself. Of course, not all the small grains disappear completely and at any given time the snowpack or column has a distribution of grain sizes and impurity concentrations. But the overall trend is an exclusion of impurities from snow grain interiors to their surfaces.

a. SO_4^{2-}

b. H^+

c. NO_3^-

d. Cl^-
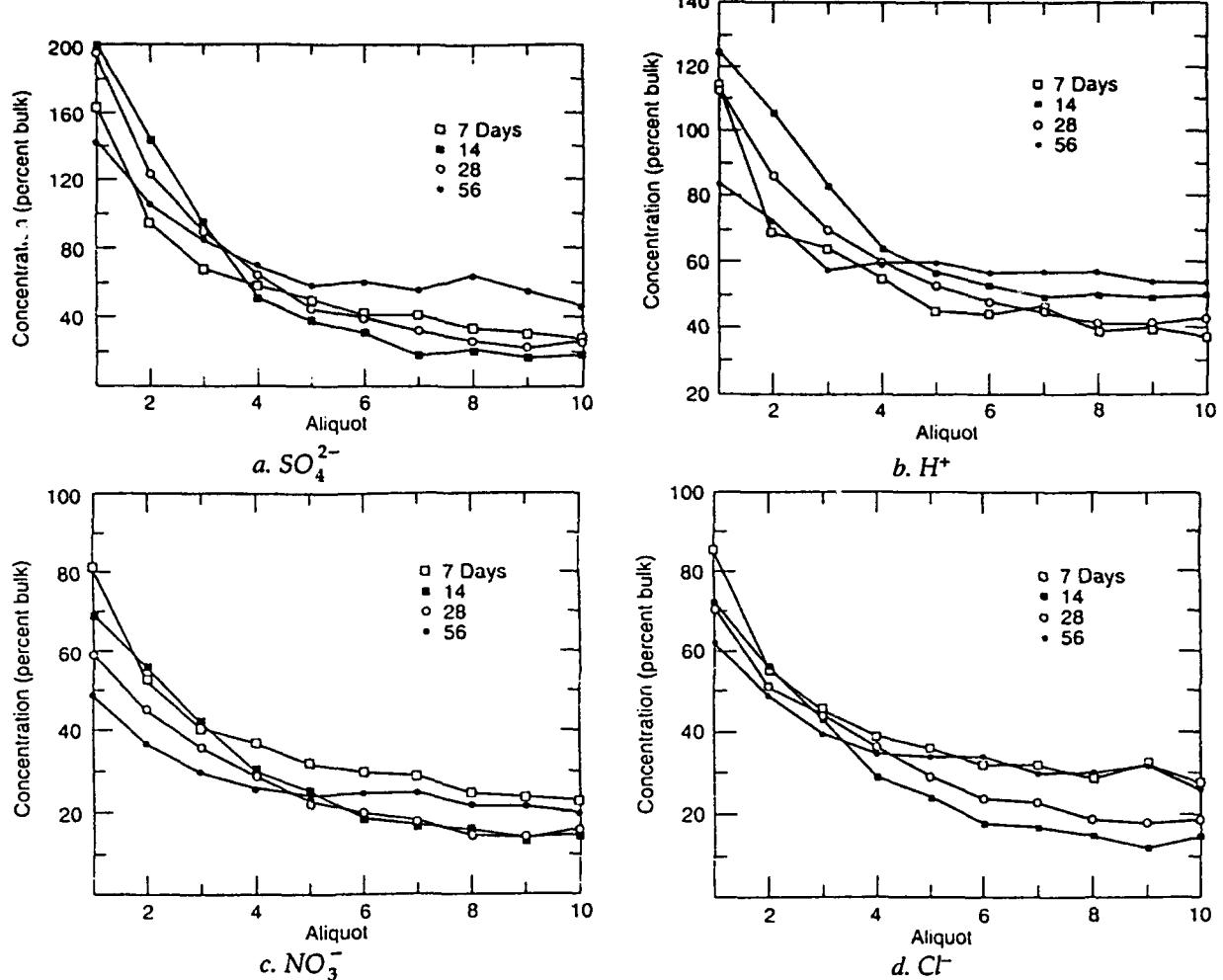
Figure 17. Concentrations of SO_4^{2-}, H^+, NO_3^- and Cl^- in initial aliquots of eluate from snow aged for 7, 14, 28, and 56 days.
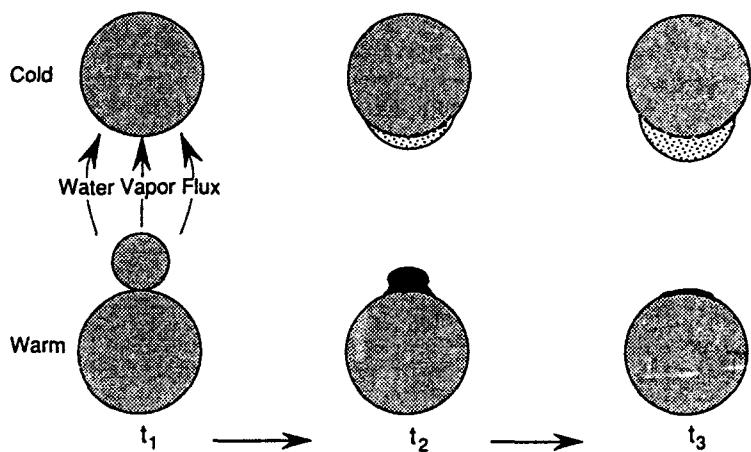
Figure 18. Theoretical depiction of chemical changes occurring during snow metamorphosis. Assume initially (time t_1) that all snow grains have similar solute concentrations (represented by shading). As water vapor moves from warmer to colder surfaces, solutes within the shrinking grains (time t_2) become concentrated. At time t_3, some grains have completely sublimed, leaving their solute load upon the surface of the larger grains.

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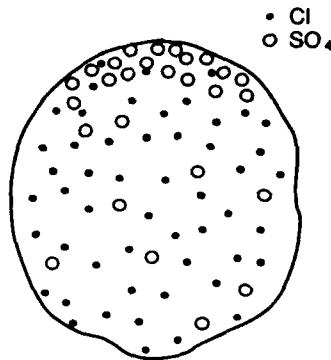
Figure 19. Hypothetical distribution of SO_4^{2-} and Cl^- within a mature, aged snow grain that has grown by vapor deposition at the bottom. The selective exclusion/retention of chemical species during metamorphosis results in snow grains with enriched surface concentrations, especially of insoluble ions such as SO_4^{2-}

The extent of this exclusion, or conversely inclusion within the growing ice grain matrix, depends upon the chemical species or ion, i.e.; it is preferential. The process is analogous to the exclusion of ions from a freezing salt solution: less soluble salts, such as sulfates, are more efficiently excluded than more soluble chlorides (Gross 1968; Gross et al. 1975). Accordingly, a mature or well metamorphosed snow grain (Fig. 19) would have higher sulfate concentrations and SO_4^{2-}/ Cl^- ratios on its surface than within its interior. The more efficiently excluded ions are more highly enriched on the snow grain surfaces and thus appear sooner and in higher concentrations in the elution water.

Preferential exclusion should also result in changing eluate ionic ratios with time. This is manifested most clearly for the SO_4^{2-}/ NO_3^- ratio (Fig. 20), which generally increases progressively as the snow age increases.

Average ratios of the three anions for the first five eluate aliquots are given in Table 4. The normalized SO_4^{2-}/ NO_3^- ratio increases from 1.8 for snow aged

Table 4. Average normalized ionic ratios for initial melt-water eluate aliquots.

Normalized ratio	Age (days)			
	7	14	28	56
SO_4^{2-}/NO_3^-	1.8	2.4	2.7	2.8
SO_4^{2-}/Cl^-	1.7	2.4	2.5	2.1
NO_3^-/Cl^-	0.9	1.0	0.8	0.8

for 7 days to 2.8 for the same snow aged for 56 days, indicating that sulfate is excluded more efficiently than nitrate. The average normalized SO_4^{2-}/Cl^- ratio increases from 1.7 to 2.5 between 7 and 28 days but then drops to 2.1 for the 56-day-old snow. This indicates that at least initially, sulfate is excluded more efficiently than chloride. But why the drop in the SO_4^{2-}/Cl^- ratio between 28 and 56 days? It is not caused by higher chloride levels because concentrations of this ion in the eluate aliquots (Fig. 17d) decrease. Also the average normalized NO_3^-/Cl^- ratio remains constant between 28 and 56 days and in fact does not deviate appreciably from unity for the four aging periods. A closer look at the ionic concentration curves in Figure 17 reveals that the degree of fractionation does not increase with sample age for all ions. For the initial aliquots, sulfate concentrations increase from 7 to 14 days, show little change between 14 and 28 days, and are lower at 56 days. So the lower SO_4^{2-}/Cl^- ratio at 56 days could be attributed to lower sulfate concentrations. Now the question becomes: why do sulfate concentrations decrease at 56 days and, further, why do they remain stable instead of increasing between 14 and 28 days? An influential factor, we believe, is the type and shape of the snow crystals themselves. At 28 and 56 days (Fig. 14 and 15) the snow crystals are not just larger but highly faceted and sintered as well. It is reasonable to expect that percolating water would rinse surface impurities from highly struc-
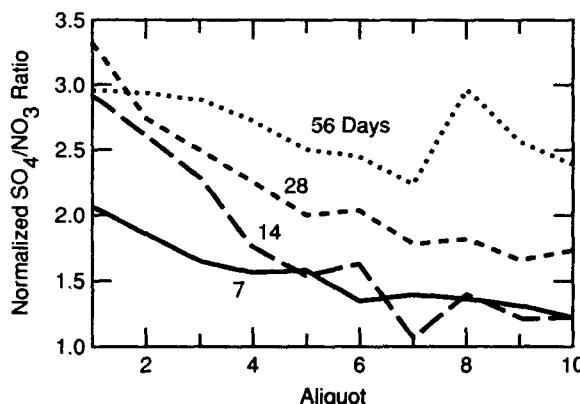

Figure 20. Individual normalized (to bulk snow) SO_4^{2-}/NO_3^- ratio for initial elution aliquots. This ratio increases with snow age because of more efficient exclusion of SO_4^{2-} than NO_3^- (or conversely less efficient inclusion of SO_4^{2-} than NO_3^-) within the ice crystal lattice during snow crystal growth.

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tured, sintered, depth hoar-like crystals less efficiently than from rounded individual crystals. Thus, in cases where a snowpack is dominated by depth-hoar-like crystals, solute release is retarded and initial chemical concentrations are lower.

These results demonstrate the effects of metamorphism upon solute release from snow that is initially chemically homogeneous. The magnitude of the ionic pulse can also be influenced by vertical variability in solute distribution (Davies et al. 1985, Bales et al. 1989, Bales 1991), diurnal melting and refreezing (Colbeck 1981, Suzuki 1991), biological activity (Jones and Deblois 1987, Jones, 1991), rainfall on snow (Tranter et al. 1992), as well as the thermal regime during snowmelt. Much of the past work has focused upon these processes which occur during snowmelt. Our studies show that dry snow processes occurring weeks and even months prior to snowmelt can also exert strong influences upon snow meltwater chemistry.

CONCLUSIONS

The initial fractions of meltwater from natural snow have ionic concentrations that are two to five times higher than that of the bulk snow from which they originate. Initial fractions of meltwater from frozen solution droplets also contain higher concentrations than the bulk solution from which they are prepared, but these fractions are two to three times less concentrated than comparable fractions from natural snowmelt. During controlled laboratory experiments ice grains did not exhibit any chromatographic sorption for chloride, nitrate or sulfate, indicating that the preferential chemical elution observed in snowpack meltwater is not due to an ion chromatographic process.

Preferential chemical elution during snowpack melting is strongly influenced by preferential chemical exclusion during snow crystal growth. Less soluble chemical impurities, such as sulfates, are excluded more efficiently and therefore appear sooner and in higher concentrations in the eluate than more soluble species, such as chloride. Snow crystal habit also influences fractionation and preferential elution both directly through different chemical release rates from crystals with different geometries and surface area volume ratios and indirectly by affecting meltwater flow rate downward through the snow. Fractionation and preferential chemical elution can result solely from dry snow metamorphism independent of other processes such as melt freeze cycles. Future efforts toward a better understanding of these processes should focus upon the simul-

taneous physical and chemical changes taking place during snow metamorphism.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE July 1993	3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE

Elution of Ions from Melting Snow:
Chromatographic Versus Metamorphic Mechanisms

5. FUNDING NUMBERS

DA: 4A161102AT24
TA: SS
WU: 002

6. AUTHORS

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755-1290

8. PERFORMING ORGANIZATION REPORT NUMBER

CRREL Report 93-8

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of the Chief of Engineers
Washington, DC 20314-1000.

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

Available from NTIS, Springfield, Virginia 22161.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Columns of natural and laboratory-aged snow grains and frozen water droplets were washed with deionized distilled water and with synthetic precipitation solutions to investigate both snowpack chemical fractionation and preferential ion elution. Concentrations of Cl^-, NO_3^- and SO_4^{2-} in sequential fractions of the column's eluate showed no chromatographic effects, indicating that ice crystals do not possess selective affinity for inorganic anions. Consequently, preferential chemical elution previously observed in melting snow is not caused by snow acting as a chromatographic column. Additional column experiments involving elution from frozen solution drops and from aged snow showed that both fractionation and preferential elution were strongly influenced by ion exclusion during the snow crystal growth.

14. SUBJECT TERMS

Acidification	Fractionation	Preferential elution
Chemical analysis	Ion exclusion	Snowmelt
Crystal growth	Meltwater	Snow metamorphosis

15. NUMBER OF PAGES
20

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL